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(54) 【発明の名称】 半導体封止用エポキシ樹脂組成物及び樹脂封止型半導体装置

## (57) 【要約】

【目的】 半導体装置の封止樹脂とインサートとの間の剥離及びクラックの発生を抑制し、耐湿性に優れた封止用樹脂組成物を提供すること。

【構成】 特定のビフェニル型エポキシ樹脂 (A成分) 及びテルペン型フェノール樹脂もしくはアラルキル型フェノール樹脂もしくはクレゾールノボラック型フェノール樹脂 (B成分)、硬化促進剤 (C成分)、無機質充填材 (D成分) を必須成分とし、前記無機質充填材を樹脂組成物に対して、60～95vol%含有してなる半導体封止用エポキシ樹脂組成物。

1

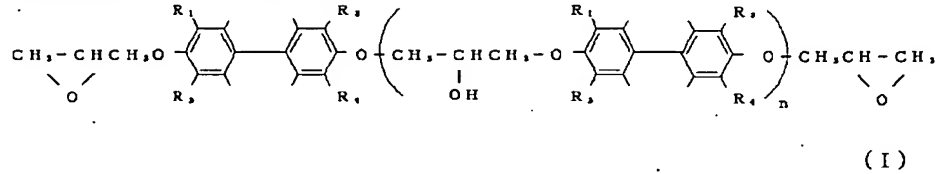
2

## 【特許請求の範囲】

【請求項1】一般式(I)で示されるビフェニル型エポキシ樹脂(A成分)、下記一般式(II)で示される水酸基当量130~180(g/eq)軟化点70~130(℃)のテルペン骨格を有するフェノール樹脂及び一般式(III)で示されるアラルキル型フェノール樹脂及び一般式(IV)で示されるクレゾールノボラック型フェノール\*

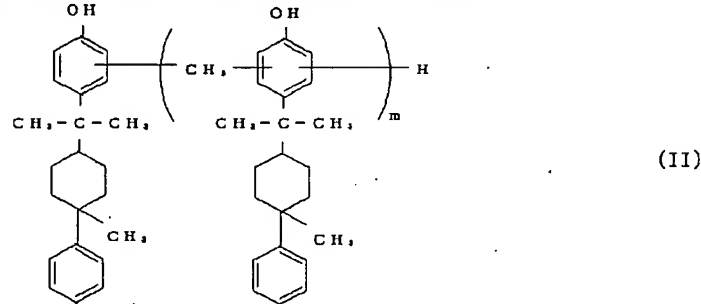
\*ル樹脂から選ばれる2種以上の硬化剤(B成分)、下記一般式(V)で示される硬化促進剤(C成分)、無機質充填材(D成分)を必須成分とし、前記無機質充填材を樹脂組成物に対して60~95vol%含有してなる半導体封止用エポキシ樹脂組成物。

## 【化1】



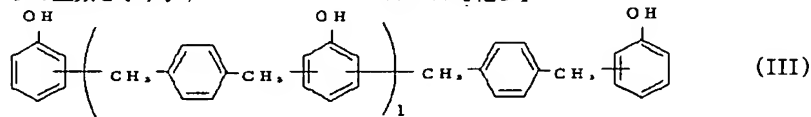
(式中、R<sub>1</sub>、R<sub>2</sub>、R<sub>3</sub>、R<sub>4</sub>は、H基、CH<sub>3</sub>基も ※す。)

しくはC(CH<sub>3</sub>)<sub>3</sub>基を示し、nは0~3の整数を示す ※ 【化2】



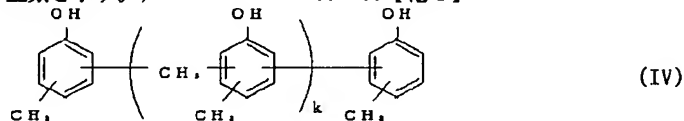
(式中、mは0~5の整数を示す。)

## ★ ★ 【化3】



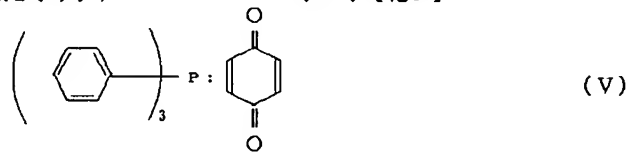
(式中、1は0~30の整数を示す。)

## ☆ ☆ 【化4】



(式中、kは0以上の整数を示す。)

## ◆ ◆ 【化5】



【請求項2】請求項1記載の半導体封止用エポキシ樹脂組成物で封止した半導体装置。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、はんだ耐熱性、耐湿性に優れた、半導体封止用エポキシ樹脂組成物及びその樹脂組成物で封止した半導体装置に関する。

## 【0002】

\*【従来の技術】IC、LSI等の半導体素子は素子の集積度の向上と共に、素子サイズ的大型化、樹脂封止型半導体装置の小型化、薄型化が進んでいる。同時に半導体装置の基板への取り付けを行う時に、半導体装置自体が短時間のうちに200℃以上の高温にさらされるようになってきた。この時、樹脂封止材中に含有される水分が気化し、ここで発生する蒸気圧が樹脂と素子、リードフレーム等のインサートとの界面において、剥離応力とし

て働き、樹脂インサートの間で剥離が発生し、特に薄型の樹脂封止型半導体装置においては、半導体装置のフレックラックに至ってしまうことになる。以上の様な剥離やクラックにより半導体装置の耐湿信頼性の劣化を生じることになる。このような剥離やクラックを生じる防止策として、タブ裏面と封止用樹脂との間の接着力を向上させるため、タブ面のディンプル加工、スリット加工等の手法が取られているが、リードフレームの高コスト化、効果不十分等の問題があり、封止用樹脂での改善が望まれる。このため、吸湿の影響が少なく、半導体装置が基板への取り付けの際の高温にさらされても、剥離やクラックが発生せず、耐湿信頼性の劣化の少ない封止用樹脂の開発が強く要求されている。

#### 【0003】

【発明が解決しようとする課題】本発明は、このような要求に対し、樹脂封止に用いる封止用樹脂組成物において、その吸湿を低下することにより、半導体装置の封止樹脂とインサートとの間の剥離及びクラックの発生を抑\*

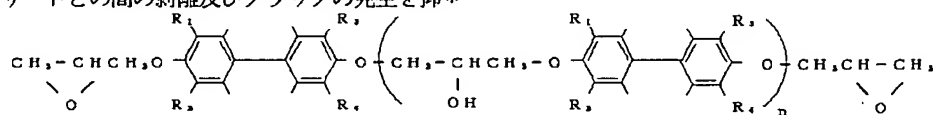
\* 制し、耐湿性に優れた封止用樹脂組成物を提供することを目的とする。

#### 【0004】

【課題を解決するための手段】本発明は、すなわち下記一般式(I)で示されるビフェニル型エポキシ樹脂(A成分)、一般式(II)で示される水酸基当量130~180(g/eq)軟化点70~130(℃)のテルペン骨格を有するフェノール樹脂一般式(III)で示されるアラルキル基フェノール樹脂及び一般式(IV)で示されるクレゾールノボラック型フェノール樹脂から選ばれる2種以上の硬化剤(B成分)、一般式(V)で示される硬化促進剤(C成分)、無機質充填材(D成分)を必須成分とし、樹脂組成物に対して前記無機質充填材を60~95vol%含有することを特徴とする半導体封止用エポキシ樹脂組成物に関する。

#### 【0005】

#### 【化1】

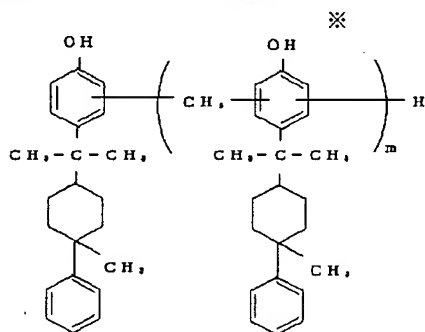


(I)

(式中、R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub> は、H基、CH<sub>3</sub> 基もしくはC(CH<sub>3</sub>)<sub>3</sub> 基を示し、nは0~3の整数を示す。)

#### ※【0006】

#### 【化2】

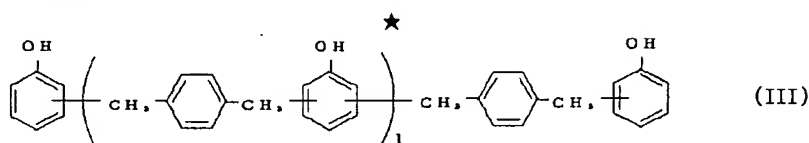


(II)

(式中、mは0~5の整数を示す。)

#### 【0007】

#### ★【化3】

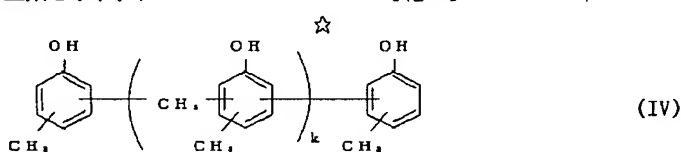


(III)

(式中、1は0~30の整数を示す。)

#### 【0008】

#### ☆【化4】

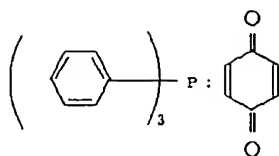


(IV)

(式中、kは0以上の整数を示す。)

#### ◆50◆【0009】

【化5】



(V)

【0010】更に、上記A成分のエポキシ樹脂には通常の半導体封止用エポキシ樹脂組成物に用いられるエポキシ樹脂を併用することができる。この併用されるエポキシ樹脂は、1分子中に2個以上のエポキシ基を有するエポキシ樹脂であれば特に制限するものではないが、従来から半導体封止用樹脂組成物の封止樹脂として用いられているオルソクレゾールノボラック型エポキシ樹脂、フェノールノボラック型エポキシ樹脂、ビフェニル型エポキシ樹脂等が好適である。

【0011】本発明に用いる上記の一般式(II)で示される水酸基当量130~180(g/e q)軟化点70~130(°C)のテルペン骨格を有するフェノール樹脂及び一般式(III)で示されるアラルキル基フェノール樹脂及び一般式(IV)で示されるクレゾールノボラック型フェノール樹脂以外にも通常の半導体封止用エポキシ樹脂組成物に用いられるフェノール樹脂を併用することができる。この併用されるフェノール樹脂は1分子中に2個以上の水酸基を有するフェノール樹脂であれば特に限定するものではないが、従来から半導体の封止樹脂として用いられているノボラック型フェノール樹脂、フェノール類とジメトキシパラキシレンから合成されるキシリレン基を有するフェノール・アラルキル樹脂、分子内にジシクロペンタジエン骨格構造を有するフェノール樹脂等があり、2種類以上併用しても良い。また、(A)のエポキシ樹脂と(B)の硬化剤の当量比(Bの水酸基数/エポキシ樹脂基数)は、特に限定はされないが、それぞれの未反応分を少なく抑えるために0.7~1.3の範囲に設定することが好ましい。

【0012】C成分の硬化促進剤として、従来使用していたアミン類及びその誘導体又はそれらの塩類、1,8-ジアザビシクロ(5,4,0)ウンデセン-7及びその誘導体又はそれらの塩類、各種オニウム化合物、イミダゾール等の硬化促進剤から一般式(IV)で示される潜在性のある(活性化エネルギーに変曲点があり、低温で反応が遅く、高温で反応が早い)硬化促進剤を用いる。C成分の硬化促進剤を必須成分として用いる一つの理由としては、上記1,8-ジアザビシクロ(5,4,0)ウンデセン-7を使用すると、成形する前に吸湿した場合、硬化性が著しく低下してしまう為である。硬化促進剤の配合割合は、好ましくはエポキシ樹脂100重量部に対して、0.1~10重量部である。

【0013】本発明に用いるD成分の無機質充填剤は結晶シリカ、溶融シリカ、アルミナ、ジルコン、珪酸カル\*

\*シウム、炭酸カルシウム、又はこれらを球形化したビーズ等が挙げられ、1種以上用いることができる。充填剤の配合量としては、成形性、熱膨張係数の低減、高温強度向上の観点から60~95vol%以上が好ましい。

【0014】その他の添加剤として高級脂肪酸、高級脂肪金属塩、エステル系ワックス、ポリエチレン系ワックス等の離型剤、カーボンブラック等の着色剤、エポキシシラン、アミノシラン、ウレイドシランビニルシラン、アルキルシラン、有機チタネート、アルミニウムアルコール等のカップリング剤及び難燃剤等を用いることができる。

【0015】以上のような原材料を用いて樹脂組成物を作製する一般的な方法としては、所定の配合量の原材料をミキサー等によって十分混合した後、ミキシングロール、押出機等によって混練し、冷却、粉碎することによって封止用樹脂組成物を得ることができる。

【0016】本発明で得られる樹脂組成物を用いて電子部品を封止する方法としては、低圧トランスファー成形法が最も一般的であるが、インジェクション成形法、圧縮成形法によっても可能である。

【0017】

【効果】前記した樹脂組成物は、低吸水性、高接着で、高温時での曲げ強度や歪みが高く、この樹脂組成物を用いて封止した半導体装置は、含有する水分が少なく、更にインサートとの密着性が高くなり、はんだ付け時のクラックが発生することなく、耐熱信頼性に優れた樹脂封止型半導体装置を提供することができる。

【0018】

【実施例】以下実施例及び比較例によって具体的に本発明を説明するが、本発明の範囲はこれらの実施例に限定されるものではない。まず、表1に示す重量部で配合し予備混合(ドライブレンド)した後、10インチ径の二軸加熱ロールを使用して、混練温度80~90℃、混練時間7~10分の条件で混練し、冷却後、粉碎後微粒化して得た封止用樹脂組成物を用いた。

【0019】実施例1~4、比較例1~6

この封止用樹脂組成物を用い、トランスファー成形機で、金型温度180℃、成形圧力70kgf/cm<sup>2</sup>、硬化時間90秒の条件で成形した。スパイラルフロー(SF)は、EMMI1-66に準じて測定した。吸湿後の硬化性については、封止用樹脂組成物を25℃、50%RH雰囲気中に24時間放置後、上記と同様にスパイラルフロー測定時カル部の硬化状態を見た。表2にお

いて、○印は、吸湿後の硬化性が良好、×印は不良であることを示す。A1ピール接着力は、厚み約0.03mmのアルミホイル上に幅10mmの成形品を上記の条件で成形し、更に175℃、5時間後硬化を行ったものについて、アルミ箔と成形品の密着力を測定した。曲げ弾性率、曲げ強さ、歪みは、127×12.7×4mmの試験片を上記の条件で成形し、更に後硬化を行ったものについて、オートグラフ（島津製作所製）を用いて、三点支持の曲げ試験を20℃及び215℃で行った。吸湿率はφ50×3mmの円板を上記の条件で成形し、更に後硬化を行ったものについてPCT（121℃、2atm）20時間後の重量変化から測定した。また、封止用樹脂組成物を用いて、半導体素子をトランスファー成形機で同様の条件で成形し、後硬化（175℃/5時間）後はんだ付け時の耐熱性と耐熱信頼性を測定した。はんだ付け時の耐熱性に用いた半導体装置QFP80ピンは、外形寸法が20×14×2（mm）のフラットパッケージであり、8×14×0.4（mm）の素子を搭載した80ピン、42アロイリードのものである。試験条件は、85℃/85%RHで所定時間加湿した後、215℃のペーパーフェーズリフロー炉において90秒加熱\*

\*する。評価は外観を顕微鏡にて観察し、パッケージクラックの有無を判定することにより行った。耐湿信頼性に用いた半導体装置DIP16ピンは、外形寸法が6.3×19.5×3.8（mm）であり、リードフレームは42アロイ材で7.2×3.9（mm）のチップサイズを有するものである。（チップのデザインはA115μm幅、ギャップ5μm、パッシベーションなし）

このようにして得られた半導体装置について、125℃、24時間ベーキング後85℃/85%RHで72時間加熱させた後、215℃のペーパーフェーズリフロー炉において、90秒加熱処理を行い、PCT（121℃、2atm）の条件化で放置した時の半導体装置のA1配線の腐食断線を導通試験を行うことにより求めた。上記の各試験結果をまとめて表2に示す。表2より、実施例の成形品は、低吸水性、高接着時での曲げ弾性率が低く、高温時での曲げ強度や歪みが高く、これを用いて封止した半導体装置は、はんだ付け時の耐熱性、耐湿信頼性が良好であることが明白である。

【0020】

【表1】

項 目	単位	実 施 例				比 較 例					
		1	2	3	4	1	2	3	4	5	6
A成分 *1		85	85	85	85	—	85	85	85	85	85
エポキシ樹脂		—	—	—	—	85	—	—	—	—	—
B(1)成分 *2		15	15	15	15	15	15	15	15	15	15
B(2)成分 *3		42	—	42	—	—	84	—	—	—	42
B(3)成分 *4		—	35	—	—	—	—	70	—	—	—
B(4)成分 *5		42	42	—	42	—	—	—	84	—	42
B(5)成分 *6		—	—	28	28	—	—	—	—	56	—
フェノールノボラック樹脂		—	—	—	—	49	—	—	—	—	—
C成分 *6	phr	3.5	3.5	3.5	3.5	—	3.5	3.5	3.5	3.5	—
1,8-ジブチルジシロキシ(5,4,0)シラン		—	—	—	—	2.5	—	—	—	—	7
シランカップリング剤		8	8	8	8	8	8	8	8	8	8
カルナウバワックス		2	2	2	2	2	2	2	2	2	2
三酸化アンチモン		6	6	6	6	6	6	6	6	6	6
カーボンブラック		3	3	3	3	3	3	3	3	3	3
熔融シリカ		1880	1810	1750	1750	1550	1880	1880	1880	1620	1910
充填材量	VOL%	83	83	83	83	83	83	83	83	83	83

\*1 A成分は本文中の式(I)のエポキシ樹脂(R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub>, R<sub>4</sub>はCH<sub>3</sub>基、

n=0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000

\*2 B(1)成分は本文中の式(II)の硬化剤（水酸基当量 178g/eq. 軟化点 128℃）

\*3 B(2)成分は本文中の式(II)の硬化剤（水酸基当量 145g/eq. 軟化点 83℃）

\*4 B(3)成分は本文中の式(III)の硬化剤（水酸基当量 175g/eq. 軟化点 70℃）

\*5 B(4)成分は本文中の式(IV)の硬化剤（水酸基当量 117g/eq. 軟化点 76℃）

\*6 C成分は本文中の式(V)の硬化促進剤

【0021】

※50※【表2】

項 目	単位	実 施 例				比 較 例					
		1	2	3	4	1	2	3	4	5	6
スパイラルフロー (S F)	inch	35	35	35	38	5	40	40	30	30	35
A 1 ビール接着力	gf/cm	550	550	550	600	成 形 不 可	450	450	550	550	550
曲げ弾性率	室温	Kgf/mm2	2600	2600	2600		2500	2500	2850	2850	2600
曲げ強さ		%	16	16	16		16	16	19	19	16
歪み	215℃	%	0.7	0.7	0.7		0.7	0.7	0.8	0.8	0.7
曲げ弾性率		Kgf/mm2	80	80	80		80	80	130	130	80
曲げ強さ		%	1.5	1.5	1.5		1.5	1.5	1.4	1.4	1.5
歪み		%	1.9	1.9	1.9		2.1	2.1	1.4	1.4	1.9
吸水率 (PCT20時間)	wt%	0.24	0.24	0.24	0.30		0.24	0.24	0.30	0.30	0.24
吸湿後の硬化性	—	○	○	○	○		○	○	○	○	×
半田付け時 の耐熱性	加 48h	PKG クラック数 /PKG数	0/5	0/5	0/5		0/5	0/5	0/5	0/5	0/5
	湿 72h		0/5	0/5	0/5		0/5	0/5	0/5	0/5	0/5
	時 96h		0/5	0/5	0/5		2/5	2/5	0/5	0/5	0/5
	間 120h		2/5	2/5	2/5		5/5	5/5	3/5	4/5	3/5
耐湿信頼性 (不良が50%発生した時間)	h	1000 以上	1000 以上	1000 以上	1000 以上		1000 以上	1000 以上	1000 以上	1000 以上	1000 以上

【0022】

【発明の効果】本発明の半導体封止用エポキシ樹脂組成物は、はんだ付け時の耐熱性、耐湿信頼性に優れたもの\*

\*であり、従って該封止用樹脂封止組成物で封止した半導体装置もはんだ付け時の耐熱性、耐湿信頼性に優れたものとなる。

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C08G 59/62

C08G 59/40

C08K 3/00

C08L 63/00

H01L 23/29

H01L 23/31

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(71)Applicant : HITACHI CHEM CO LTD

(22)Date of filing : 18.05.1995

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**(54) EPOXY RESIN COMPOSITION FOR SEALING SEMICONDUCTOR AND RESIN-SEALED TYPE SEMICONDUCTOR DEVICE**

(57)Abstract:

PURPOSE: To obtain the subject composition comprising a biphenyl type epoxy resin of a specific structure, two or more kinds of curing agents, a curing promoter and an inorganic filler as essential components, excellent in heat resistance of solder and moisture resistance.

CONSTITUTION: This epoxy resin composition comprises (A) a biphenyl type epoxy resin of formula I [R1 to R4 are each H, CH3 or C(CH3)3; n is an integer of 0-3], (B) two or more kinds of curing agents selected from a terpene skeleton- containing phenol resin of formula II (m is an integer of 0-5) having 130-180g/eq. hydroxyl group equivalent and 70-130°C softening point, an aralkyl type phenol resin of formula III ((1) is an integer of 0-30) and a cresol novolak type phenol resin of formula IV (k is an integer of  $\geq 0$ ) (C) a curing promoter of formula V and (D) 60-95vol.% based on the composition of an inorganic filler as essential components. The equivalent ratio of the component A and the component B is preferably 0.7-1.3. The blending ratio of the component C is preferably 0.1-10 pts.wt. based on 100 pts.wt. of the component A.

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1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. \*\*\*\* shows the word which can not be translated.

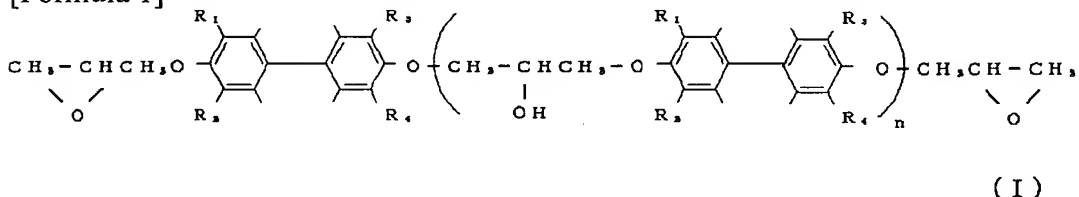
3. In the drawings, any words are not translated.

## CLAIMS

[Claim(s)]

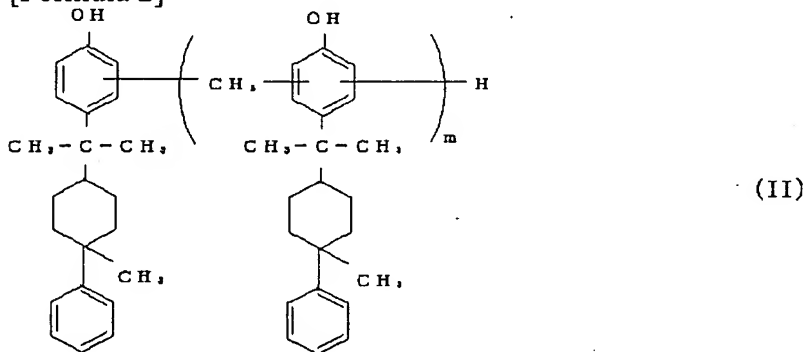
[Claim 1] The biphenyl mold epoxy resin shown by the general formula (I) (A component), The following general formula The hydroxyl equivalents 130-180 shown by (II) (g/eq) The phenol resin and the general formula (III) which have the terpene frame of softening temperatures 70-130 (degree C) Two or more sorts of curing agents chosen from the cresol novolak mold phenol resin shown by the aralkyl mold phenol resin and the general formula (IV) which are shown (B component), the hardening accelerator (C component) and minerals filler (D component) which are shown by the following general formula (V) -- an indispensable component -- carrying out -- said minerals filler -- a resin constituent -- receiving -- 60 - 95vol% -- the epoxy resin constituent for the semi-conductor closures which it comes to contain.

[Formula 1]



(The inside of a formula, R1, R2, R3, and R4 are H sets, CH3 radical, or C(CH3)3. A radical is shown and n shows the integer of 0-3)

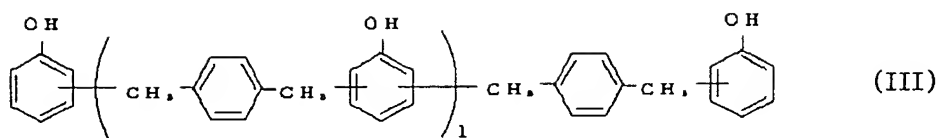
[Formula 2]



(m shows the integer of 0-5 among a formula.)

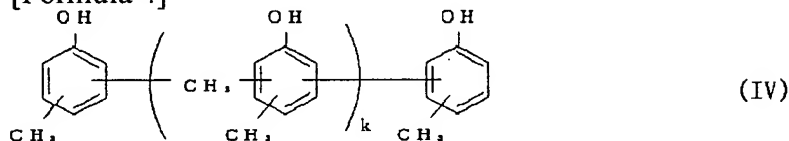
[Formula 3]





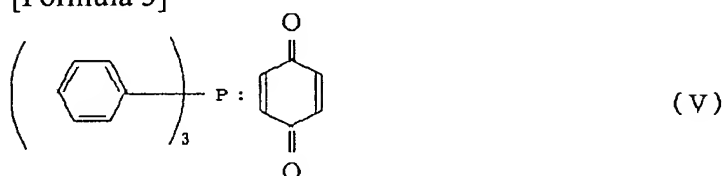
(1 shows the integer of 0-30 among a formula.)

[Formula 4]



(k shows zero or more integers among a formula.)

[Formula 5]



[Claim 2] The semiconductor device closed with the epoxy resin constituent for the semiconductor closures according to claim 1.

[Translation done.]

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3. In the drawings, any words are not translated.

## DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the semiconductor device closed with the epoxy resin constituent for the semi-conductor closures excellent in solder thermal resistance and moisture resistance, and its resin constituent.

[0002]

[Description of the Prior Art] As for semiconductor devices, such as IC and LSI, enlargement of component size, the miniaturization of a plastic molded type semiconductor device, and thin shape-ization are progressing with improvement in the degree of integration of a component. When performing installation to the substrate of a semiconductor device to coincidence, the semiconductor device itself has come to be exposed to an elevated temperature 200 degrees C or more in the inside of a short time. At this time, the moisture contained in a resin sealing agent will evaporate, and the vapor

pressure generated here works as exfoliation stress in the interface of resin and an insertion of a component, a leadframe, etc., and between resin insertions, exfoliation will occur and it will keep in blistering and the crack of a semiconductor device very much in a thin plastic molded type semiconductor device especially. Degradation of the humidity-tolerant reliability of a semiconductor device will be produced by the above exfoliations and cracks. Although technique, such as dimple processing of a tab side and slit processing, is taken as a preventive measure which produces such exfoliation and a crack in order to raise the adhesive strength between a tab rear face and the resin for the closures, there are problems, such as a raise in the cost of a leadframe and insufficiency of effectiveness, and an improvement with the resin for the closures is desired. For this reason, even if there is little effect of moisture absorption and it is exposed to the elevated temperature in the case of the installation to a substrate of a semiconductor device, neither exfoliation nor a crack occurs but development of the resin for the closures with little degradation of humidity-tolerant reliability is demanded strongly.

[0003]

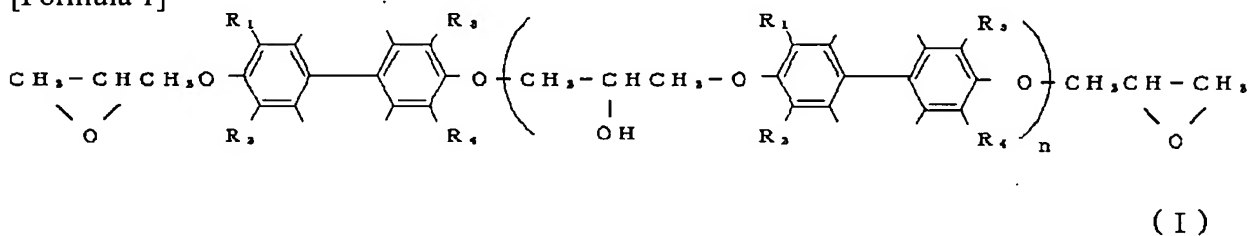
[Problem(s) to be Solved by the Invention] To such a demand, by falling the moisture absorption in the resin constituent for the closures used for a resin seal, this invention controls the exfoliation between the closure resin of a semiconductor device, and an insertion, and generating of a crack, and aims at offering the resin constituent for the closures excellent in moisture resistance.

[0004]

[Means for Solving the Problem] The biphenyl mold epoxy resin shown by this invention (I), i.e., the following general formula, (A component), A general formula The hydroxyl equivalents 130-180 shown by (II) (g/eq) Phenol resin general formula which has the terpene frame of softening temperatures 70-130 (degree C) (III) Two or more sorts of curing agents chosen from the cresol novolak mold phenol resin shown by the aralkyl radical phenol resin and the general formula (IV) which are shown (B component), the hardening accelerator (C component) and minerals filler (D component) which are shown by the general formula (V) -- an indispensable component -- carrying out -- a resin constituent -- receiving -- said minerals filler -- 60 - 95vol% -- it is related with the epoxy resin constituent for the semi-conductor closures characterized by containing.

[0005]

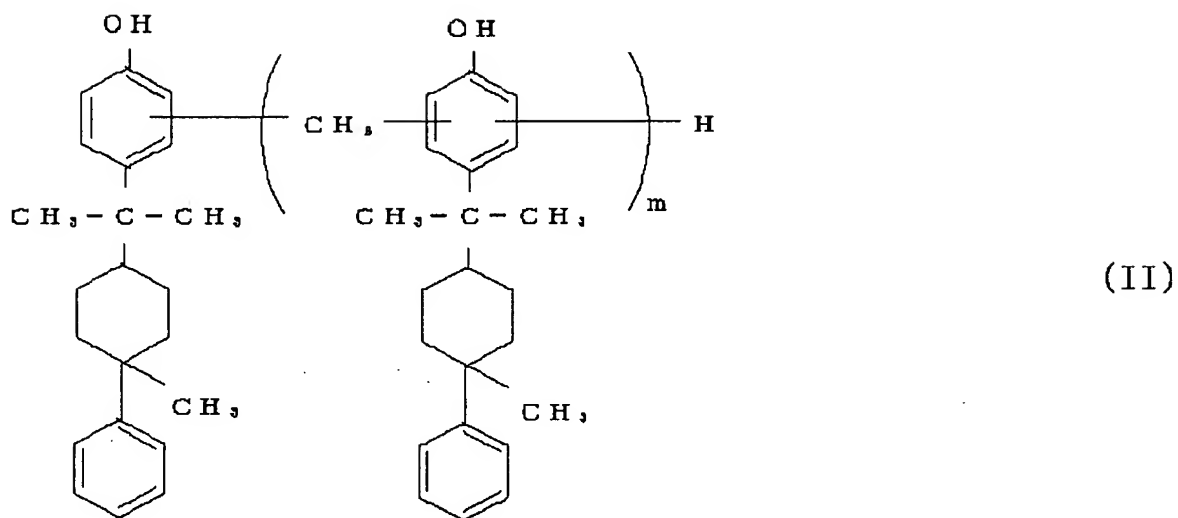
[Formula 1]



(The inside of a formula, R1, R2, R3, and R4 are H sets, CH3 radical, or C(CH3)3. A radical is shown and n shows the integer of 0-3)

[0006]

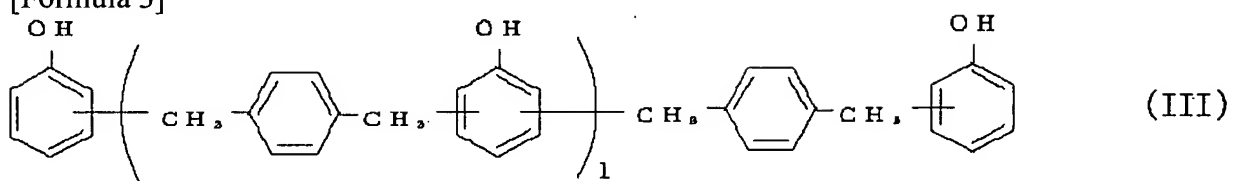
[Formula 2]



(m shows the integer of 0-5 among a formula.)

[0007]

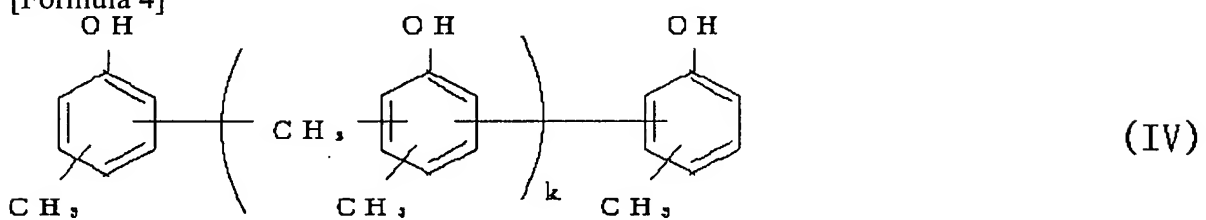
[Formula 3]



(l shows the integer of 0-30 among a formula.)

[0008]

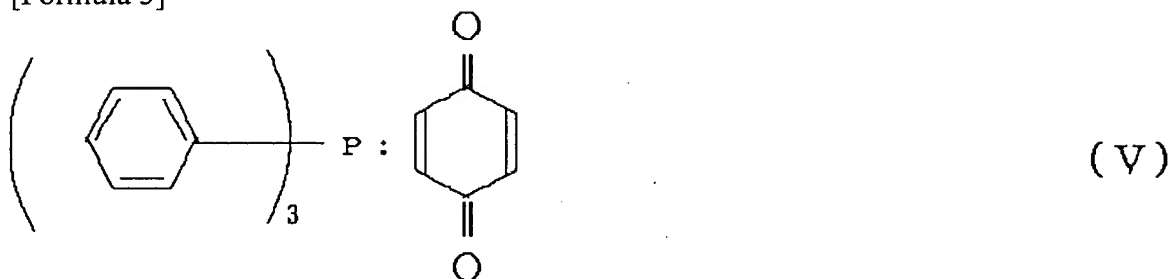
[Formula 4]



(k shows zero or more integers among a formula.)

[0009]

[Formula 5]



[0010] Furthermore, to the epoxy resin of the above-mentioned A component, the epoxy resin used for the usual epoxy resin constituent for the semi-conductor closures can be used together. Although this epoxy resin used together is not restricted especially if it is an epoxy resin which has two or more epoxy groups in 1 molecule, the polyglycidyl ether of o-cresol-form aldehyde novolac used as closure resin of the resin constituent for the semi-conductor closures from the former, a phenol novolac mold epoxy resin, a biphenyl mold epoxy resin, etc. are suitable for it.

[0011] The phenol resin and the general formula (III) which have the terpene frame of the hydroxyl equivalent 130 shown by the above-mentioned general formula (II) used for this invention - 180 (g/eq) softening temperatures 70-130 (degree C) The phenol resin used for the usual epoxy resin constituent for the semi-conductor closures besides the cresol novolac mold phenol resin shown by the aralkyl radical phenol resin and the general formula (IV) which are shown can be used together. Although this phenol resin used together is not limited especially if it is phenol resin which has two or more hydroxyl groups in 1 molecule, from the former, it has the novolac mold phenol resin used as closure resin of a semi-conductor, the phenol aralkyl resin which has the xylylene radical compounded from phenols and dimethoxy paraxylene, phenol resin which has dicyclopentadiene skeletal structure in intramolecular, and may be used together two or more kinds. moreover -- although especially limitation is not carried out for the equivalent ratio (the number of hydroxyl groups / epoxy resin of B base) of the epoxy resin of (A), and the curing agent of (B) -- each -- unreacted -- a part -- in order to stop few, it is desirable to set it as the range of 0.7-1.3.

[0012] A hardening accelerator with the latency shown by the general formula (IV) as a hardening accelerator of C component from hardening accelerators, such as amines [ which were being used conventionally ] and its derivative or those salts, 1, and 8-diazabicyclo (5, 4, 0) UNDENSEN -7 and its derivative or those salts, various onium compounds, and an imidazole, (point of inflection is in activation energy, a reaction is slow at low temperature, and a reaction is early at an elevated temperature) is used. When the above 1 and 8-diazabicyclo (5, 4, 0) UNDENSEN -7 were used and it absorbs moisture as one reason using the hardening accelerator of C component as an indispensable component before fabricating, it is for hardenability to fall remarkably. The blending ratio of coal of a hardening accelerator is 0.1 - 10 weight section to the epoxy resin 100 weight section preferably.

[0013] A crystal silica, fused silica, an alumina, zircon, a calcium silicate, a calcium carbonate, or the bead that conglobated these is mentioned, and one or more sorts of minerals bulking agents of D component used for this invention can be used. As loadings of a bulking agent, more than 60-95vol% is desirable from a viewpoint of reduction of a moldability and a coefficient of thermal expansion, and the improvement in high temperature strength.

[0014] A coupling agent, flame retarders, etc., such as coloring agents, such as release agents, such as a higher fatty acid, a high-class fat metal salt, an ester system wax, and a polyethylene system wax, and carbon black, an epoxy silane, an amino silane, ureido silane vinylsilane, an alkyl silane, organic titanate, and aluminum alcoholate, can be used as other additives.

[0015] As a general approach of producing a resin constituent using the above raw materials, after mixing the raw material of predetermined loadings enough by a mixer etc., the resin constituent for the closures can be obtained by kneading and grinding [ cool and ] with a roll mill, an extruder, etc.

[0016] As an approach of closing electronic parts using the resin constituent obtained by this invention, although the low voltage transfer-molding method is the most common, it is possible also by the injection fabricating method and compression forming.

[0017]

[Effect] The plastic molded type semiconductor device excellent in heat-resistant dependability can be offered without the above mentioned resin constituent having the flexural strength in the time of an elevated temperature, and a high distortion at low water absorption and high adhesion, the semiconductor device closed using this resin constituent having little moisture to contain, adhesion with an insertion becoming high further, and the crack at the time of soldering occurring.

[0018]

[Example] Although an example and the example of a comparison explain this invention concretely below, the range of this invention is not limited to these examples. First, after blending and carrying out preliminary mixing (dryblend) in the weight section shown in Table 1, the 2 shaft heating roller of the diameter of 10 inch was used, it kneaded on the kneading temperature of 80-90 degrees C, and the conditions for mixing time 7 - 10 minutes, and the resin constituent for the closures which atomized after cooling and grinding and was obtained was used.

[0019] examples 1-4 and the examples 1-6 of a comparison -- it fabricated with the transfer-molding machine using this resin constituent for the closures on the die temperature of 180 degrees C, compacting pressure 70 kgf/cm<sup>2</sup>, and the conditions for setting-time 90 seconds. Spiral flow (SF) was measured according to EMMI 1-66. About the hardenability after moisture absorption, the hardening condition of the cull section was seen for the resin constituent for the closures like the above after 24-hour neglect in 25 degrees C and 50%RH ambient atmosphere at the time of spiral flow measurement. In Table 2, O mark shows that fitness and x mark have the poor hardenability after moisture absorption. A1 Peel adhesive strength fabricated mold goods with a width of face of 10mm on the above-mentioned conditions on aluminum foil with a thickness of about 0.03mm, and measured the adhesion force of aluminum foil and mold goods about 175 more degrees C and the thing which performed postcure for 5 hours. A bending elastic modulus, bending strength, and distortion fabricated the 127x12.7x4mm test piece on the above-mentioned conditions, and performed the bending test of a three point suspension at 20 degrees C and 215 degrees C about what performed postcure further using the autograph (Shimadzu make). Moisture absorption fabricated the phi50x3mm disk on the above-mentioned conditions, and measured it about what performed postcure further from the weight change 20 hours after PCT (121 degrees C, 2atm). Moreover, using the resin constituent for the closures, the semiconductor device was fabricated with the transfer-molding machine on the same conditions, and the thermal resistance at the time of postcure (175-degree-C / 5 hours) back soldering and heat-resistant dependability were measured. A dimension is the flat package of 20x14x2 (mm), and semiconductor device QFP80 pin used for the thermal resistance at the time of soldering is the thing of 80 pins and 42 alloy lead which carried the component of 8x14x0.4 (mm). A test condition is

heated for 90 seconds in a 215-degree C vapor phase reflow furnace, after carrying out predetermined time humidification by RH 85 degrees C / 85%. Evaluation observed the appearance under the microscope and was performed by judging the existence of a package crack. The dimension of semiconductor device DIP16 pin used for humidity-tolerant reliability is 6.3x19.5x3.8 (mm), and a leadframe has the chip size of 7.2x3.9 (mm) by 42 alloy material. (The design of a chip has A115-micrometer width-of-face and gap 5micrometer and no passivation)

Thus, about the obtained semiconductor device, after making it heat by RH for 72 hours after [ 24 hour baking ] 85 degrees C / [ 125 degrees C and ], and 85%, in the 215-degree C vapor phase reflow furnace, heat-treatment was performed for 90 seconds, and it asked for the corrosion open circuit of A1 wiring of the semiconductor device when leaving it in conditioning of PCT (121 degrees C, 2atm) by performing a continuity check. Each above-mentioned test result is collectively shown in Table 2. The mold goods of an example have low water absorption and a low bending elastic modulus in the time of high adhesion, the flexural strength in the time of an elevated temperature and distortion are high, and, as for the semiconductor device closed using this, it is clearer than Table 2 that the thermal resistance at the time of soldering and humidity-tolerant reliability are good.

[0020]

[Table 1]

項 目	単位	実 施 例				比 較 例					
		1	2	3	4	1	2	3	4	5	6
A成分 *1		85	85	85	85	—	85	85	85	85	85
メタクリレート-メタクリレート型エポキシ樹脂		—	—	—	—	85	—	—	—	—	—
B r 化エビヒス型エポキシ樹脂		15	15	15	15	15	15	15	15	15	15
B (1) 成分 *2		42	—	42	—	—	84	—	—	—	42
B (2) 成分 *3		—	35	—	—	—	—	70	—	—	—
B (3) 成分 *4		42	42	—	42	—	—	—	84	—	42
B (4) 成分 *5		—	—	28	28	—	—	—	—	56	—
フェノールノボラック樹脂		—	—	—	—	48	—	—	—	—	—
C成分 *6	phr	3.5	3.5	3.5	3.5	—	3.5	3.5	3.5	3.5	—
1,8-ジブチルシクロ(5,4,0)ノナデセン-7		—	—	—	—	2.5	—	—	—	—	7
シランカップリング剤		8	8	8	8	8	8	8	8	8	8
カルナウバワックス		2	2	2	2	2	2	2	2	2	2
三酸化アンチモン		6	6	6	6	6	6	6	6	6	6
カーボンブラック		3	3	3	3	3	3	3	3	3	3
熔融シリカ		1880	1810	1750	1750	1550	1880	1880	1880	1620	1910
充填材量	VOL%	83	83	83	83	83	83	83	83	83	83

- \*1 A成分は本文中の式 (I) のエポキシ樹脂 ( $R_1, R_2, R_3, R_4$ は $CH_3$ 基、 $n = 0, 24$  相当量 192g/eq. 軟化点 110°C)
- \*2 B (1) 成分は本文中の式 (II) の硬化剤 (水酸基当量 178g/eq. 軟化点 128°C)
- \*3 B (2) 成分は本文中の式 (II) の硬化剤 (水酸基当量 145g/eq. 軟化点 83°C)
- \*4 B (3) 成分は本文中の式 (III) の硬化剤 (水酸基当量 175g/eq. 軟化点 70°C)
- \*5 B (4) 成分は本文中の式 (IV) の硬化剤 (水酸基当量 117g/eq. 軟化点 76°C)
- \*6 C成分は本文中の式 (V) の硬化促進剤

[0021]  
[Table 2]

項 目	単位	実 施 例				比 較 例					
		1	2	3	4	1	2	3	4	5	6
スパイラルフロー (SF)	inch	35	35	35	38	5	40	40	30	30	35
A1ピール接着力	gf/cm	550	550	550	600	成 形 不 可	450	450	550	550	550
曲げ弾性率	室温	Kgf/mm <sup>2</sup>	2600	2600	2600		2500	2500	2850	2850	2600
曲げ強さ			16	16	16		16	16	19	19	16
歪み		%	0.7	0.7	0.7		0.7	0.7	0.8	0.8	0.7
曲げ弾性率	215℃	Kgf/mm <sup>2</sup>	80	80	80		80	80	130	130	80
曲げ強さ			1.5	1.5	1.5		1.5	1.5	1.4	1.4	1.5
歪み		%	1.9	1.9	1.9		2.1	2.1	1.4	1.4	1.9
吸水率 (PCT20時間)	wt%		0.24	0.24	0.24		0.24	0.24	0.30	0.30	0.24
吸湿後の硬化性	—		○	○	○		○	○	○	○	×
半田付け時の耐熱性	加 48h	PKG クラック数 /PKG数	0/5	0/5	0/5		0/5	0/5	0/5	0/5	0/5
	湿 72h		0/5	0/5	0/5		0/5	0/5	0/5	0/5	0/5
	時 86h		0/5	0/5	0/5		2/5	2/5	0/5	0/5	0/5
	間 120h		2/5	2/5	2/5		5/5	5/5	3/5	4/5	3/5
耐湿信頼性 (不良が50%発生した時間)	h		1000 以上	1000 以上	1000 以上		1000 以上	1000 以上	1000 以上	1000 以上	1000 以上

[0022]  
[Effect of the Invention] The epoxy resin constituent for the semi-conductor closures of this invention becomes what excelled [ semiconductor device / which was excellent in the thermal resistance at the time of soldering, and humidity-tolerant reliability, therefore was closed with this resin seal constituent for the closures ] in the thermal resistance at the time of soldering, and humidity-tolerant reliability.

[Translation done.]

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(21)Application number : 06-274051 (71)Applicant : ASAHI DENKA KOGYO  
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**CLAIMS**

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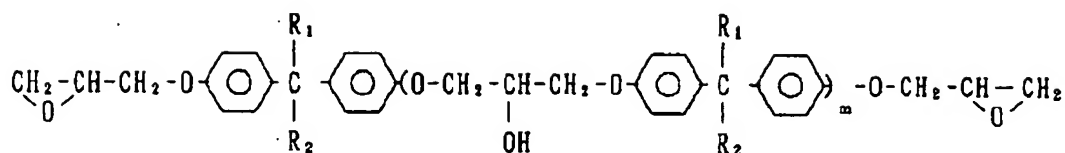
[Claim(s)]

[Claim 1] (A) To a kind of epoxy resin chosen from the group which the carbon atomic number of the joint hand which combines the poly glycidyl ether and each nucleus of a single nucleus polyhydric phenol becomes from the poly glycidyl ether of four or less polykaryotic polyhydric phenol, at least (B) the terpene soil skeleton content phenolic compound which is made to add a phenol or an alkylphenol compound to an annular terpene compound, and is obtained The epoxy resin constituent containing the resultant made to add to one epoxy group of the above-mentioned epoxy resin (A) by the ratio from which the phenolic hydroxyl group of the above-mentioned terpene soil skeleton content phenolic compound (B) becomes 0.05-0.8 pieces whose weight per epoxy equivalent is 200-2000.

[Claim 2] The epoxy resin constituent according to claim 1 whose above-mentioned epoxy resin (A) is an alkylidene bisphenol poly glycidyl ether mold epoxy resin expressed with the general formula of following [-ized 1].

[Formula 1]





(式中、R<sub>1</sub>およびR<sub>2</sub>は各々独立に水素原子またはアルキル基を示し、mは0～2を示す。)

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[Translation done.]

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the epoxy resin constituent which can give the good paint film of the weatherability and anti-corrosiveness which were meltable to TAPEN (terpene hydrocarbon oil) which is a high-boiling point and a low stimulative solvent with high safety, and were excellent in it, hardenability, and the adhesion to various base materials.

[0002]

[Description of the Prior Art] Since it excels in the adhesive property over various base materials, thermal resistance, chemical resistance, an electrical property, a mechanical characteristic, etc., the epoxy resin is especially used widely as a coating, adhesives, etc.

[0003] Although the thing of the solvent type which dissolved the epoxy resin in various kinds of low-boiling point solvents was common when using it for these applications, from problems, such as a bad influence to the danger of a fire, the harmful nature to the body, and earth environment, use of a low-boiling point solvent comes to be restricted, and the change to a high-boiling point and low stimulative solvents, such as reduction-izing of a solvent or TAPEN, came to be called for strongly.

[0004] However, since the epoxy resin or phenol novolak mold epoxy resin manufactured from bisphenol A or Bisphenol F currently conventionally used widely, and epichlorohydrin is inferior to the solubility to TAPEN, when using it as a solvent type, a high-boiling point and low stimulative TAPEN were not able to be used. For this reason, it was meltable to TAPEN and to find out the epoxy resin excellent in the adhesive property over various base materials, corrosion resistance, thermal resistance, chemical

resistance, the electrical property, the mechanical characteristic, etc. was desired strongly. [0005] The epoxy resin obtained by the reaction of the condensate of the terpene soil skeleton content polyhydric-phenol compound or this polyhydric-phenol compound which adds phenols to an annular terpene compound and is obtained, and aldehydes, and epichlorohydrin is proposed by JP,4-45121,A, JP,4-117420,A, and JP,5-222155,A, and since this epoxy resin is excellent in electric insulation, thermal resistance, low absorptivity, etc., it is indicated especially that it is useful to the electrical and electric equipment and the laminate in an electronic application.

[0006] The epoxy resin guided from the above-mentioned terpene soil skeleton content polyhydric-phenol compound was not what may be satisfied with using it for the coating field as which there is a fault inferior to the degree of hardness of a hardening coat, corrosion resistance, alkali resistance, hardenability, etc., and these properties are required of, although the solubility over TAPEN was good.

[0007] Moreover, although the above-mentioned epoxy resin and the polyhydric-phenol conversion epoxy resin to which polyhydric-phenol compounds, such as bisphenol A, were made to react were proposed by JP,4-359920,A, also when such conversion was performed, the corrosion resistance, alkali resistance, hardenability, etc. were not what may be satisfied.

[0008] Moreover, the suitable hardenability epoxy resin constituent for the semiconductor closures which using a terpene soil skeleton content polyhydric-phenol compound as a curing agent of an epoxy resin is also proposed, for example, mixed the terpene soil skeleton content polyhydric-phenol compound with the epoxy resin of the diglycidyl ether mold of bisphenols to JP,4-26642,A and JP,4-55422,A is indicated.

[0009] However, in this way, when a terpene soil skeleton content polyhydric-phenol compound was only mixed with the epoxy resin of an alkylidene bisphenol poly glycidyl ether mold, most solubility over TAPEN of an epoxy resin had the degree of hardness of a hardening coat, corrosion resistance, alkali resistance, hardenability, the inadequate adhesion to a base material, etc., and it is not not only improved, but was not what it may simply be satisfied with using it for the coating field of.

[0010] Therefore, the purpose of this invention is to offer the epoxy resin constituent which is excellent in weatherability, anti-corrosiveness, alkali resistance, hardenability, and adhesion, and it not only excels in the solubility over TAPEN which can be used suitable for the application of the object for coatings especially a heavy anticorrosive paint, white top coat, etc., but can give a coat with the degree of hardness of a hardening coat big moreover.

[0011]

[Means for Solving the Problem] The epoxy resin constituent containing the resultant to which the terpene soil skeleton content phenolic compound which is made to add phenols to a polyhydric-phenol poly glycidyl ether mold epoxy resin and an annular terpene compound as a result of this invention persons' repeating examination wholeheartedly, and is obtained was made to add by the specific ratio carried out the knowledge of the ability to attain the above-mentioned purpose.

[0012] At least this invention to a kind of epoxy resin chosen from the group which it was made based on the above-mentioned knowledge, and the carbon atomic number of the joint hand which combines the poly glycidyl ether and each nucleus of (A) single nucleus polyhydric phenol becomes from the poly glycidyl ether of four or less

polykaryotic polyhydric phenol (B) the terpene soil skeleton content phenolic compound which is made to add a phenol or an alkylphenol compound to an annular terpene compound, and is obtained Contain the resultant made to add by the ratio from which the phenolic hydroxyl group of the above-mentioned terpene soil skeleton content phenolic compound (B) becomes 0.05-0.8 pieces to one epoxy group of the above-mentioned epoxy resin (A). Weight per epoxy equivalent offers the epoxy resin constituent which are 200-2000.

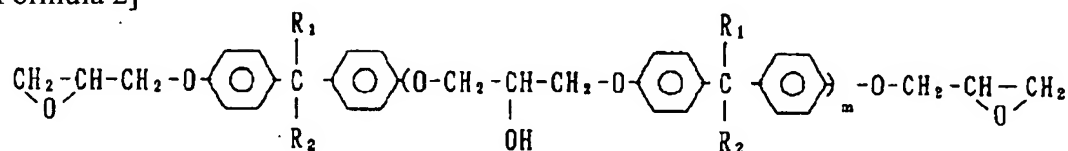
[0013] Hereafter, the epoxy resin constituent of this invention is explained to a detail.

[0014] The epoxy resin of the (A) component used for this invention It is a kind of epoxy resin chosen from the group which the carbon atomic number of the joint hand which combines the poly glycidyl ether and each nucleus of a single nucleus polyhydric phenol becomes from the poly glycidyl ether of four or less polykaryotic polyhydric phenol at least. As this epoxy resin, for example Hydroquinone, resorcinol, methyl resorcinol, Single nucleus polyhydric-phenol compounds, such as a pyrocatechol and FUROROGURUKUSHI Norian; Dihydroxy naphthalene, Biphenol, a methylenebis phenol (bisphenol F), methylenebis (orthochromatic cresol), An ethylidene bisphenol, an isopropylidene bisphenol (bisphenol A), An isopropylidene screw (orthochromatic cresol), tetra-bromine bisphenol A, 1, 3-screw (4-hydroxy cumyl benzene), 1, 4-screw (4-hydroxy cumyl benzene), 1, 1, 3-tris (4-hydroxyphenyl) butane, 1, 1 and 2, 2-tetrapod (4-hydroxyphenyl) ethane, Novolaks, such as polykaryotic polyhydric-phenol compound; phenol novolaks, such as a thio bisphenol, a sulfo bisphenol, and an oxy-bisphenol, an orthochromatic cresol novolak, and a resorcinol novolak; poly glycidyl ether is raised.

[0015] When the alkylidene bisphenol poly glycidyl ether mold epoxy resin especially expressed with the general formula of following [-ized 2] (it is the same as the above [-izing 1]) is used also in the above-mentioned epoxy resin, since it excels in corrosion resistance, weatherability, the adhesion to a base material, etc., it is desirable.

[0016]

[Formula 2]



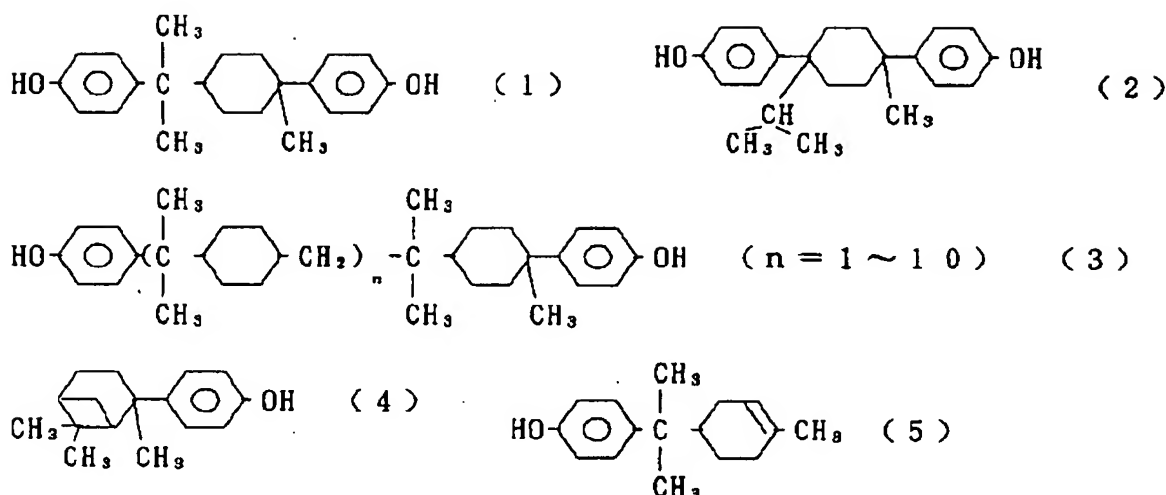
(式中、R<sub>1</sub>およびR<sub>2</sub>は各々独立に水素原子またはアルキル基を示し、mは0～2を示す。)

[0017] The inside of the above-mentioned formula, and R1 And R2 As an alkyl group shown, the alkyl group of the carbon atomic numbers 1-8, such as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, hexyl, heptyl, and octyl, is raised.

[0018] The terpene skeletal structure content phenolic compound of the (B) component used for this invention adds alkylphenol compounds, such as a phenol or orthochromatic cresol, to an annular terpene compound, it is obtained, and the compound expressed with following type [ of [-izing 3] ] (1) - (5) is raised.

[0019]

[Formula 3]



[0020] This invention is a thing containing the resultant which made the terpene soil skeleton content phenolic compound of the above-mentioned (B) component add to the epoxy resin of the above-mentioned (A) component. Both As opposed to one epoxy group of an epoxy resin (A) the phenolic hydroxyl group of a terpene soil skeleton content phenolic compound (B) 0.05-0.8 pieces, When using a mono-phenolic compound as the ratio which becomes 0.1-0.7 pieces preferably, especially a terpene soil skeleton content phenolic compound (B), it is used by the ratio which becomes 0.1-0.5 pieces preferably. By using the above-mentioned terpene soil skeleton content phenolic compound (B) by such ratio, it comes out of the content of the resultant which the above in the constituent of this invention made add preferably to consider as 30 % of the weight or more still more preferably 20% of the weight or more. Since weight per epoxy equivalent becomes remarkably large in the solubility to TAPEN becoming inadequate and exceeding the above-mentioned range in the case of under the range (they are less than 0.05 hydroxyl groups to one epoxy group) of the above [ the rate of an use rate of the above-mentioned terpene soil skeleton content phenolic compound (B) ] (it is 0.8 hydroxyl-groups \*\* to one epoxy group), since there are few contents of the above-mentioned resultant, hardenability becomes inadequate and alkali resistance, corrosion resistance, etc. become inadequate.

[0021] The approach of being able to adopt the usual method of making a phenolic compound adding to an epoxy resin as an approach of making the above-mentioned (B) component adding to the above-mentioned (A) component, and acquiring a resultant, for example, heating both at 60-200 degrees C under existence of basic catalysts, such as dimethyl benzylamine, etc. can be used.

[0022] As for the epoxy resin constituent of this invention obtained as mentioned above, weight per epoxy equivalent needs 200-2000, and to be 230-1500 preferably. If the above-mentioned weight per epoxy equivalent becomes insufficient [ less than 200 / the solubility to TAPEN ] and exceeds 2000, hardenability will become inadequate and alkali resistance, corrosion resistance, etc. will become inadequate.

[0023] Generally, a curing agent is blended and the epoxy resin constituent of this invention is used for the application of a coating, adhesives, etc.

[0024] As the above-mentioned curing agent, especially if usually used as a curing agent

for epoxy resins, it is possible to use it, without receiving a limit, for example, aromatic series, aliphatic series or heterocycle type polyamine and those poly epoxide addition conversion objects, an amidation conversion object, a MANNIHHI-ized conversion object, etc. can be used if needed. Also in these curing agents, since a basic curing agent can harden an epoxy resin at a room temperature or low temperature, it is suitable for using for the epoxy resin constituent of this invention.

[0025] As the above-mentioned polyamine, aromatic series polyamine, such as heterocycle type polyamine, such as an alicyclic polyamine [ , such as polyalkylene poly MIAN such as diethylenetriamine, triethylenetetramine, and tetraethylenepentamine, 1, 2-diamino cyclohexane, 1, the 4-diamino -3, 6-diethyl cyclohexane, and isophorone diamine, ], 1, and 4-bis(3-aminopropyl) piperazine, m-xylylene diamine, diamino diphenylmethane, and diaminodiphenyl sulfone, is raised, for example. The above-mentioned poly epoxide addition conversion object Moreover, the above-mentioned polyamine, phenyl glycidyl ether, Butyl glycidyl ether, bisphenol A-diglycidyl ether, It is manufactured by making various kinds of epoxy resins, such as glycidylethers, such as bisphenol F-diglycidyl ether, or glycidyl ester of a carboxylic acid, react with a conventional method. The above-mentioned amidation conversion object is manufactured by making the above-mentioned polyamine and carboxylic acids, such as dimer acid, react with a conventional method. The above-mentioned MANNIHHI-ized conversion object It is manufactured by making the phenols which have the aldehyde-reaction point of a piece at least react to nuclei, such as the above-mentioned polyamine, aldehydes, such as formaldehyde, and a phenol, cresol, a xyleneol, the third butylphenol, and resorcinol, with a conventional method.

[0026] Moreover, in using the epoxy resin constituent of this invention as a coating, although a solvent is blended, usually Although it has the description that the epoxy resin constituent of this invention is meltable to a high-boiling point and low stimulative TA-pen with high safety, i.e., spirit of turpentine, D-limonene, a pinene, etc., and these can be used as a dilution solvent Other common solvents, for example, a commercial high-boiling point hydrocarbon system solvent, can also be used. It could be mixed and this high-boiling point hydrocarbon system solvent may consist [ the high-boiling point hydrocarbon system solvents of aliphatic series, an alicycle group, and aromatic series, or / these ] of a single presentation of a xylene, a mesitylene, etc. Furthermore, it replaces with some or all of these high-boiling point hydrocarbon system solvents, an acetone, toluene, a methyl ethyl ketone, ethyl acetate, propylene glycol mono-ethyl ether, N,N-dimethylformamide, N,N-dimethylacetamide, ethyl acetate, etc. can be used, and these solvents can also be used for arbitration as two or more sorts of partially aromatic solvents.

[0027] It responds to the epoxy resin constituent of this invention at the need. Moreover, monoglycidyl ether Dioctyl phthalate, dibutyl phthalate, benzyl alcohol, A diluent (plasticizer) reactant [ , such as a coal tar, ] or nonresponsive, a glass fiber, A carbon fiber, a cellulose, silica sand, cement, a kaolin, clay, an aluminum hydroxide, A bentonite, a silica, an impalpable powder silica, a titanium dioxide, carbon black, Additives in ordinary use, such as bulking agents, such as graphite and ferrous oxide, or a pigment, a thickener, a CHIKISOTORO pick agent, a flame retarder, and a defoaming agent, may be contained, and adhesive resin, such as xylene resin and petroleum resin, can also be further used together.

[0028] The epoxy resin constituent of this invention is used, the additive of requests, such as a filler, is added to an epoxy resin constituent as an approach of preparing a coating, according to a conventional method, and the method of putting in a glass bead and kneading with a predetermined time shaker etc. is raised. The obtained coating can make a paint film form by applying and carrying out desiccation hardening by predetermined thickness using a bar coating machine etc., after mixing a curing agent.

[0029]

[Example] Although the example of this invention is shown below, this invention is not limited to these. In addition, among each example, with weight per epoxy equivalent, it defines as the molecular weight of the epoxy resin per epoxy group, and is defined as OH equivalent with the molecular weight of the terpene skeletal structure frame content phenolic compound per phenolic hydroxyl group.

[0030] To example 1 thermometer, stirring equipment, a cooling pipe, and 500 cc 4 Thu opening round bottom flask equipped with the nitrogen inlet ADEKA resin EP-4901 (; by Asahi Denka Kogyo K.K. -- a bisphenol female mold epoxy resin --) weight-per-epoxy-equivalent 175 144.0g (0.82eq) and terpene phenol copolymer YP-90LL (the Yasuhara Chemical, Inc. make --) Dimethyl benzylamine 0.17g is taught as average molecular weight 266, OH equivalent 300 26.6g (0.09eq, 0.11 hydroxyl groups per epoxy group), and a catalyst. After carrying out the temperature up of the inside of a system to 120 degrees C, it was made to react for 2.5 hours and the terpene soil skeleton content phenol conversion epoxy resin of weight per epoxy equivalent 250, and the viscosity 133ps / the shape of 25-degree C yellow liquid was obtained.

[0031] To example 2 thermometer, stirring equipment, a cooling pipe, and 500 cc 4 Thu opening round bottom flask equipped with the nitrogen inlet ADEKA resin EP-4100 (; by Asahi Denka Kogyo K.K. -- the bisphenol A mold epoxy resin --) Weight-per-epoxy-equivalent 190 190.0g (1.00eq), terpene phenol copolymer YP-90LL60.0g (0.20 eq) Dimethyl benzylamine 0.39g is taught as 0.20 hydroxyl groups per epoxy group, and a catalyst. After carrying out the temperature up of the inside of a system to 120 degrees C, it was made to react for 3 hours and the terpene soil skeleton content phenol conversion epoxy resin of weight per epoxy equivalent 350, and the viscosity 4650ps / the shape of 25-degree C yellow liquid was obtained.

[0032] To example 3 thermometer, stirring equipment, a cooling pipe, and 500 cc 4 Thu opening round bottom flask equipped with the nitrogen inlet 190.0g (1.00eq) ADEKA resin EP-4100, 115.0 g (0.38 eq) Dimethyl benzylamine 0.39g is taught as terpene phenol copolymer YP-90LL of 0.38 hydroxyl groups per epoxy group, and a catalyst. After carrying out the temperature up of the inside of a system to 120 degrees C, it was made to react for 3 hours and the terpene soil skeleton content phenol conversion epoxy resin of the yellow solid-state of weight per epoxy equivalent 500 was obtained.

[0033] To example 4 thermometer, stirring equipment, a cooling pipe, and 500 cc 4 Thu opening round bottom flask equipped with the nitrogen inlet 75g terpene diphenol copolymer YP-90 (the Yasuhara Chemical, Inc. make --) which uses as a principal component the compound expressed with the formula (1) shown in ADEKA resin EP-4901 of (0.43eq), ADEKA resin EP-4100 [ 40g (0.21eq) ], and the above [-izing 3], and/or (2) Average molecular weight 324, the OH equivalent 162, 85-degree-C melting point of 75g (0.46 eq) After teaching dimethyl benzylamine 0.17g as 0.72 hydroxyl groups per epoxy group, and a catalyst and carrying out the temperature up of the inside

of a system to 120 degrees C, it was made to react for 4 hours and the terpene soil skeleton content phenol conversion epoxy resin of the yellow solid-state of weight per epoxy equivalent 1050 was obtained.

[0034] To example 5 thermometer, stirring equipment, a cooling pipe, and 500 cc 4 Th opening round bottom flask equipped with the nitrogen inlet phenol novolak epoxy resin DEN431 (made in Dow Chemical Company --) 2.2 average functional groups, weight-per-epoxy-equivalent =175 144g (0.82eq), Terpene phenol copolymer YP-90LL92g (0.31 eq) After teaching dimethyl benzylamine 0.36g as 0.38 hydroxyl groups per epoxy group, and a catalyst and carrying out the temperature up of the inside of a system to 120 degrees C, it was made to react for 3 hours and the terpene soil skeleton content phenol conversion epoxy resin of the yellow solid-state of weight per epoxy equivalent 480 was obtained.

[0035] 162g taught the 11. reactor equipped with example of comparison 1 thermometer, stirring equipment, and a cooling pipe YP-90, epichlorohydrin 740g and 1.1g of tetraethyl ammonium chloride catalysts were added, and it heated at 117 degrees C, and was made to react under reflux for 2 hours. Subsequently, this was cooled to 60 degrees C, the water decollator was attached, 42g NaOH was added, and it was made to react at 50-70 degrees C under reduced pressure of 40 - 100mmHg. Azeotropy of the water generated during a reaction was carried out to epichlorohydrin, it removed, and the reaction terminal point was made into the about 2-hour back the time of theoretical water measurement distilling. Methyl-isobutyl-ketone (MIBK) 2500cc was added to the epichlorohydrin solution of the obtained epoxy resin, and after removing the salt and superfluous NaOH which were washed and generated with a lot of water, the phosphate water solution neutralized 3%. Subsequently, epichlorohydrin and MIBK were distilled off by the evaporator and 196g of terpene soil skeleton content epoxy resins of weight per epoxy equivalent 233 was obtained.

[0036] Added dimethyl benzylamine 0.3g to the 11. reactor equipped with example of comparison 2 thermometer, stirring equipment, and a cooling pipe as 66g (0.28eq) of terpene soil skeleton content epoxy resins, 18g (0.16eq) of bisphenol A, and the catalyst of the example 1 of a comparison, it was made to react to it at 150 degrees C for 3 hours, and the terpene soil skeleton content epoxy resin of weight per epoxy equivalent 700 was obtained.

[0037] Taught 175g (1.00eq) ADEKA resin EP-4901 and 74g (0.65eq) of bisphenol A to the reactor equipped with example of comparison 3 thermometer, stirring equipment, and a cooling pipe, it was made to react to it at 150 degrees C for 2.5 hours, and the epoxy resin of weight per epoxy equivalent 700 was obtained.

[0038] ADEKA resin EP-4901 and 26.6 g (0.09eq) terpene phenol copolymer YP-90LL of the 4144.0 g (0.82eq) example of a comparison were blended in 25-degree C ordinary temperature, and the epoxy resin constituent containing a terpene soil skeleton content phenol was obtained.

[0039] They are ADEKA resin EP-4901 [ 75g (0.43eq) ], ADEKA resin EP-4100 [ 40g (0.21eq) ], and 89g (0.55 eq) to the reactor equipped with example of comparison 5 thermometer, stirring equipment, and a cooling pipe. Taught dimethyl benzylamine 0.18g as YP-90 and the catalyst of 0.86 hydroxyl groups per epoxy group, after carrying out the temperature up of the inside of a system to 130 degrees C, it was made to react for 7 hours, and the terpene polyhydric-phenol conversion epoxy resin of the yellow solid-state

of weight per epoxy equivalent 2250 was obtained.

[0040] 100g of epoxy resin constituents obtained in examples 1-5 and the examples 1-5 of a comparison was dissolved in 100g of every spirits of turpentine, and the solubility was obtained. Soluble evaluation is performed by the following three-stage, and the result is shown in following [table 1].

O : it dissolves in homogeneity and insoluble matter is not accepted.

\*\* : A small amount of insoluble matter is accepted.

x : A lot of insoluble matter is accepted.

[0041]

[Table 1]

ターペン溶解性試験結果

	実 施 例					比 較 例				
	1	2	3	4	5	1	2	3	4	5
溶解性	○	○	○	○	○	○	△	×	×	○

[0042] Using the epoxy resin constituent obtained in the above-mentioned examples 1-5 and the examples 1-5 of a comparison, according to the following combination, it kneaded with the shaker for 2 hours, and the white coating was prepared using the glass bead.

[0043]

(Combination)

Epoxy resin constituent 20 Weight section titanium dioxide 20 bentonites 1 spirit of turpentine 14.1 Solvesso 100 3.5 (high-boiling point hydrocarbon solvent by Exxon chemistry incorporated company).

[0044] As a curing agent, the Addie Kaha-donor EH340 (Asahi Denka Kogyo K.K. make; a conversion polyamide amine, active hydrogen equivalent 81) was blended with the obtained white coating so that it might become an epoxy group / curing agent active hydrogen = 1/1 equivalent ratio of an epoxy compound, and it considered as the coating constituent.

[0045] Subsequently, the obtained coating constituent is applied so that it may become Thickness 30-50micro on a metal plate using a 070 bar coating machine, at 25 degrees C, it was left on the 7th and desiccation hardening was carried out. The property of the obtained paint film test piece is evaluated as following, and those results are shown in following [table 2].

[0046] In addition, the approach of each performance evaluation is as follows.

\*\* Erichsen; it carried out on conditions (phi20mm and 8mm) using the Erichsen test machine.

\*\* An alkali-proof trial; JIS It is based on K-5400.

\*\* Corrosion resistance test; JIS It carried out based on K-5400, having sandblasting plate paint film covered it over SST for 500 hours. A criterion is as follows.

The flat-surface section O ; Rust and have no blister. \*\* ; \*\* -- it sees a little -- x ; \*\* -- it sees mostly -- Cross-cut section O ; It rusts. 0.5mm or less of blisters O -\*\* ; \*\* 0.5-1mm \*\* ; \*\* 1-1.5mm \*\*-x ; \*\* 1.5-2mm x ; \*\* 2mm or more \*\* weathering test; it is JIS about a mild steel plate paint film test piece. At 60 degrees C, the gloss before and behind 200-hour exposure was measured with the glossmeter (mirror reflectivity of 60 degrees) to B-7752UV contest equipment, and the gloss retention was computed to it.



\*\* Cold cure nature; finger touch estimated the existence of tacking when leaving it at 10 degrees C after spreading for 15 hours, and it evaluated in two steps, O and x.

\*\* Aluminum adhesion; JIS The aluminum plate specified to H-4000 was used, and also the paint film test piece was created similarly, the cross cut was put into the paint film, the tape friction test was performed to it, and the peeling condition of a paint film was compared with it.

O ; -- peeling-less \*\* ; -- a part -- x as which peeling is regarded ; [0047] in which the whole surface separates

[Table 2]

白色塗膜試験結果

試験項目		実 施 例					比 較 例				
		1	2	3	4	5	1	2	3	4	5
エリクセン		○	○	○	○	○	○	△	△	△	×
耐アルカリ性（24時間）		○	○	○	○	○	×	△	○	△	×
耐食性	平面部	○	○	○	○	○	×	△	○	×	×
	クロスカット部	○	○	○	○	○	×	△	○	×	×
耐候性（光沢保持率％）		76	85	88	98	73	80	70	40	47	73
低温硬化性		○	○	○	○	○	×	×	○	×	×
アルミ密着性		○	○	○	○	○	○	○	×	△	×

[0048] The terpene soil skeleton content phenol conversion epoxy resin constituent (examples 1-5) which is an epoxy resin constituent of this invention is excellent in TAPEN solubility, and can form the good paint film of corrosion resistance, weatherability, and the adhesion to a base material so that clearly from an above-mentioned example and the above-mentioned example of a comparison.

[0049] On the other hand, only the result which the solubility to TAPEN is not only inferior in the epoxy resin constituent (example 4 of a comparison) which the epoxy resin constituent (example 3 of a comparison) which does not contain a terpene soil skeleton at all was inferior to the adhesion to a base material not only the solubility to TAPEN is inferior, but, and only blended the terpene soil skeleton content phenol, but was inferior by all trial items is obtained.

[0050] Even if it is a terpene soil skeleton content epoxy resin constituent, with many contents of a terpene soil skeleton The epoxy resin constituent (examples 1 and 2 of a comparison) using the epoxy compound guided from a terpene soil skeleton content polyhydric phenol Although the solubility to TAPEN is excellent, even if corrosion resistance and cold cure nature are inadequate and it is the epoxy resin constituent by which conversion was carried out with the terpene soil skeleton content phenol When there is much amount of the terpene soil skeleton content phenol used (example 5 of a comparison) (weight per epoxy equivalent is large) Although excelled in the solubility to TAPEN, only the result which was completely inferior by all trial items is obtained. It is clear that the effectiveness by having used the epoxy resin constituent (examples 1-5) of this invention which limits the amount of the terpene soil skeleton content phenol used comparatively a little, and has specific weight per epoxy equivalent is very specific.

[0051]

[Effect of the Invention] The epoxy resin constituent (claim 1) of this invention is meltable to a high-boiling point and low stimulative TAPEN with high safety, it excels in corrosion resistance, weatherability, and a water resisting property, and the adhesion to various base materials, such as vinyl chloride, aluminum, and a zinc plate, can form a good paint film. Therefore, the epoxy resin constituent (claim 1) of this invention is useful for the application of various coatings, adhesives, a sealing agent, etc. Moreover, especially the epoxy resin constituent (claim 2) of this invention is excellent in corrosion resistance, weatherability, the adhesion to a base material, etc.

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[Translation done.]